Peer Review Comments on:

# Technical Background Document:
# Mercury Wastes
# Evaluation of Treatment of Bulk Elemental Waste

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## Evaluation of Treatment of Bulk Elemental Mercury

In order to help evaluate whether EPA could propose treatment and disposal alternatives to the current land disposal restriction (LDR) treatment standard of mercury retorting, EPA conducted a study on the treatment of bulk elemental mercury. The study was performed to assess conditions that affect the stability of waste residues resulting from the treatment of bulk elemental mercury. The results of the study were submitted for formal, independent peer review by three national experts with significant technical expertise in hazardous waste leaching. These peer reviewers have no prior association with this study, and have no perceived or actual conflict with any impact of the study results. The members of the peer review panel were tasked with evaluating the adequacy of the experimental design, conduct, and conclusions of the study. The peer review panel also provided information on how the study can be used to provide a framework to determine whether additional protective measures are required to prevent loss of mercury to the environment from the treatment and co-disposal of mercury-bearing wastes in landfills. Additionally, the members of the peer review panel were asked if additional studies were warranted for other factors that impact solubility (e.g., liquid/solid ratio, redox conditions, leachate composition) or affect ability to leach (such as use of macroencapsulation). The specific questions asked of the peer reviewers are provided in this document, along with the peer reviewer's comments, and EPA's responses to those comments.

**Charge Question 1: Was the experimental design of the study appropriate?**

Reviewer #1: Yes. This study was conducted with well-defined objectives and a carefully generated study design. The test protocols and operating instructions were well developed. This study conducted controlled laboratory testing of elemental mercury stabilization offered by commercially available methods and vendors. The stabilized samples were tested for leaching in the laboratory in a replicated manner.

Reviewer #2: The design followed neither EPA guidance nor requirements for the use of Data Quality Objectives.

***Response**: EPA has developed the DQOs process as the Agency's recommended planning process when environmental data are used to select between two opposing conditions, such as achieving or not achieving a numerical standard. The DQOs process is used to develop qualitative and quantitative statements of the overall level of uncertainty that a decision-maker is willing to accept in results or decisions derived from environmental data, i.e., Data Quality Objectives. The DQOs process entails a seven step systematic procedure for defining the criteria that a data collection design should satisfy, including when to collect samples, where to collect samples, the tolerable level of decision error for the study, and how many samples to collect, balancing risk and cost in an acceptable manner. When this process is not directly applicable (i.e., the experimental objective is estimation, research, or any other objective that does not select between two distinct conditions), the Agency recommends the use of a systematic planning method for defining performance criteria. For this research project, a systematic planning method was used. A Quality Assurance Project Plan (QAPP) was developed by EPA and was followed throughout the project. EPA believes that the project objectives and criteria were logical, given the intended end-use of the data, well-defined, and achievable.*

I could not find the QAPP for this project (the included QAPP appeared identical to the QAPP for the surrogate sludge project), but it apparently dealt with only laboratory QA/QC and not the larger issues of decisions to be made, decision error, and optimizing the plan. Had this been done, the problems of treated waste inhomogeneity, sub-sampling, numbers of samples, and optimizing data collection, e.g., using composite samples, could have been incorporated into the study design. In particular, a clear statement of the decisions could have noted the importance of leaching solids up to at least pH 12.5, the regulatory limit for hazardous waste. Perhaps more important, a statement of acceptable errors should have been included, e.g., a treatment technology must be effective on 90% of wastes with a 90% confidence. Without such a statement, it is difficult to decide when a technology is good enough.

***Response**: EPA added the study on stabilization of bulk elemental mercury to an on-going study on the stabilization of mercury-contaminated surrogate waste. The study was added because of concerns about long-term disposition of the Defense Logistics Agency (DLA) mercury stockpile, and was intended to mirror the on-going study, both in experimental design and study goals. Because of this similarity in design and goals, the very limited amount of time remaining in the contract, as well as budget limitations, the decision was made to operate the bulk elemental study under the surrogate study QAPP. The heterogeneity issues experienced during the bulk elemental mercury study were very similar to those experienced during the surrogate study - they were not predicted during the planning phase of either study, and would not have been better identified in a separate planning document. The study was intended to evaluate how well the available treatment technologies performed on a level playing field, not to determine if the treatment technologies could meet a certain performance standard. Therefore, a statement of acceptable error would have been inappropriate.*

The design of leaching waste treated with mercuric selenide was not consistent with the other leaching tests and only included leaching at two pHs. As a result, the conclusion regarding the effect of chloride could not be compared with the effect of pH over a larger range.

***Response**: A technology is available that threats waste with selenium, forming mercuric selenide as the stable (insoluble) treatment residual. During the stabilization evaluation, the solubility of mercuric selenide in the presence of chloride ions was evaluated using a computer model (Minteq). The results of that modeling exercise indicated that mercuric selenide becomes soluble when exposed to chloride ions for some unknown period of time. This finding prompted EPA to add an evaluation of the stability of mercuric selenide in the constant-pH leaching test, with and without chloride ions, to evaluate solubility in the short term. This experiment was not intended to be comparable to the larger-pH range leaching tests conducted for the other treatment technologies.*

Reviewer #3: The experimental design was generally appropriate. One exception was the failure to confirm that waste loadings (elemental mercury loadings) were as reported by the vendors. The report does not present any data supporting the reported waste loadings. The experimental plan calls for mercury concentrations in the waste forms to be determined, but these data are not presented. These concentrations would be a check on the reported waste loadings and should be reported.

***Response**: That analytical plan called for the determination of waste loadings using SW-846 Method 7470A, Mercury in Liquid Waste (Manual Cold-Vapor Technique). This analytical approach yielded poor recoveries because the treatment residual was difficult to digest, making it impossible to dissolve the mercury and make it available for analysis. As a result, the waste loadings reported by the vendors could not be verified.*

Identifying the concentrations of mercury in the waste forms among the raw data in Appendix B is difficult. However, an attempt was made to identify these concentrations and it appears that the mercury contents of treated solids from some vendors were much lower than expected from reported waste loadings. The highest concentration reported for a solid from vendor A (samples 01 to 10, p B-98) is 16,400 mg/kg, compared to a concentration of 330,000 mg/kg expected from the reported waste loading of 33%. The highest concentration found for a solid treated by Vendor B (samples 34 to 43 on p B-154, B-155) is 285,000 mg/kg compared to concentrations of 550,000 mg/kg and 440,000 mg/kg expected for waste loadings of 55% (Phase I) and 44% (Phase II). Other concentrations are reported in this group that are much lower. The highest concentration found for a solid treated by Vendor C is 10,700 mg/kg (samples 9 to 13, p. B-67) compared to a concentration of 201,000 mg/kg expected for a waste loading of 20.1%.

***Response**: The reported concentration are from the analyses with incomplete digestion discussed previously, and are recognized to be lower than the "true" values. The reported waste loadings are theoretical values, based on the known masses of mercury added to know masses of additives in the treatment process.*

Recoveries of metals from treated wastes are often less than expected. Low recoveries can be the result of inadequate analytical procedures for measuring metals in solids that have been treated with the intent to reduce the availability of the metal. No information was given concerning the dissolution procedures used on the treated wastes to solubilize mercury prior to analysis. The only procedure specified (SW 846 Method 7470A) is a method for analyzing mercury in aqueous solutions. Therefore, there is no way to determine if the dissolution procedure could be expected to reliably recover mercury. Regardless of the reason for the low recoveries for treated wastes submitted by Vendors A and C, they are so low that they cast doubt on the meaningfulness of the results of leaching tests.

***Response**: The sample digestion protocol used for the solid samples is described in Appendix B, pages 207- 213. This digestion procedure follows the first digestion option provided in SW-846 Method 7471A Mercury in Solid or Semi-solid Waste (Manual Cold-Vapor Technique). The determinative portions of the two procedures are identical. Therefore, we can assume that the procedure could be expected to reliably recover mercury.*

*All spike recovery measurements of the leachates achieved quantitative recoveries between 84% and 109%. Thus, there is no evidence of a problem with the analysis of mercury in the leachates. We believe this is because the mercury was in solution, and therefore, available for analysis.*

**Charge Question 2: Was the study conducted properly?**

Reviewer #1: Most likely yes, although there are possible heterogeneity present in the stabilized wastes as indicated by large variability in concentrations in replicates subjected to leaching tests. My review of the material in the report suggests that the vendors and laboratories properly carried out the preparation of stabilized waste forms and the leaching tests required on the stabilized samples. Appropriate QA/QC and reporting of results have been accomplished.

Reviewer #2: The lab procedures appear acceptable, although I could not find detailed sampling and sub-sampling procedures. The procedures appear to have been carried out correctly.

***Response**: General sampling procedures are provided in Section 4.0 of the QAPP. Specific sampling and sub-sampling procedures were not provided, as the physical form and characteristics of the treated waste forms was not well-defined before the treatment took place. Each vendor was charged with using best professional judgement and skill at ensuring that the treated waste form submitted was representative of the bulk of the entire treated waste form. In subsampling the waste form for testing purposes, the engineers conducting the testing were similarly charged.*

Reviewer #3 The study was conducted properly, with the exception of assuring that waste loadings were as reported by the vendors.

***Response**: As discussed earlier, the analytical plan called for the determination of waste*

*loadings using SW-846 Method 7470A, Mercury in Liquid Waste (Manual Cold-Vapor Technique). This analytical approach yielded poor recoveries because the treatment residual was difficult to digest, making it impossible to dissolve the mercury and make it available for analysis. As a result, the waste loadings reported by the vendors could not be verified.*

**Charge Question 3: Were the stated objectives adequately met?**

Reviewer #1: Yes. The report specifies two major objectives as (1) to evaluate alternative treatment processes for elemental mercury to meet a TCLP treatment goal of 0.025 mg/L or less, and (2) to empirically test and compare new leaching protocols to the standard TCLP method. This study included testing of pellets and crushed samples of the stabilized/treated elemental mercury. In addition, limited evaluation was conducted to examine the effects of chloride in leaching solution on leaching of mercury from stabilized materials. The results and graphs presented in this report clearly show that there are significant differences in the effectiveness of the various treatment technologies. The constant pH leaching test results indicate that leaching of mercury from the stabilized elemental mercury is a pH dependent phenomenon. For example, Vendor B stabilized material shows a monotonic increase in mercury leaching as the leaching fluid pH is increased from highly acidic to highly alkaline. Vendor C stabilized elemental mercury shows a decreasing leaching pattern when leaching fluid pH is increased from acidic pH of 2. The Vendor A results are more variable. The leaching test results indicate that Vendor B treatment performs the best and meets the treatment goal of 0.025 mg/L leachate concentration for pH range of 2 to at least 10. The Vendor C stabilized material does not yield results that are 0.025 mg/L and/or lower. Vendor A does produce stabilized material that meets the leaching goal only at pH 2. Therefore, this study report should recognize that all treatment technologies that were tested are not equally effective, and that Vendor B technology provides the most effective method for a large range of pH conditions. This report also needs to conclude that the new leaching test protocols yield significantly different leaching concentrations than the TCLP test. This is not surprising, particularly when elemental mercury is being reacted to form a sulfide solid phase compound that is known to have pH dependent solubility.

***Response**: The intent of this study was to evaluate the stability of treatment residuals from commercially available technologies against bench mark standards, and not to compare the technologies to each other. Therefore, EPA believes that it is inappropriate to reach the relative conclusions suggested by the reviewer. The final test conditions of the TCLP were shown to be vary from waste to waste. However, TCLP leachate concentrations were consistent with the concentration gradients as a function of pH indicated by the constant pH measurements. Thus, in general, the two test procedures provided similar results when compared at the same pH level.*

Reviewer #2: The first review objective was to ”evaluate the effectiveness of alternative treatments to obtain a goal of 0.025 mg/L TCLP over a range of pH 2 to pH 12.” I assume the reference to TCLP is a mistake, and the objective is to review the results of the constant pH extraction. With this assumption, the data collected were adequate to do the evaluation, with the exception of an apparent sample heterogeneity problem.

The second review objective was to compare constant pH protocol results to standard TCLP results. The data were adequate for this comparison, with the exception of sample heterogeneity.

***Response**: EPA agrees that sample heterogeneity was a recurring issue, albeit a minor one. We believe that the sample heterogeneity is inherent in the nature of both the untreated and treated materials, and difficult to control. As the study was intended to evaluate the treatment residuals from the stabilization technologies as they are used commercially, we believe that this heterogeneity is a variable that must be considered.*

The third review objective was to evaluate the effects of increased chloride concentration of mercuric selenide at constant pH conditions. These data were not adequate since only two pHs and two chloride concentrations were used; the results were inadequate to quantitatively compare the chloride effect with the pH effect.

***Response**: As previously discussed, EPA added a resource-limited evaluation of the stability of mercuric selenide in the constant-pH leaching test, with and without chloride ions, to evaluate solubility in the short term. This experiment was not intended to be comparable to the larger-pH range leaching tests conducted for the other treatment technologies. These limited data suggest to us that the presence of chloride ions could be an important factor in the leaching behavior of stabilized mercury wastes. Therefore, we would suggest any future studies in this area include chloride as a variable.*

Reviewer #3: a) Effectiveness of meeting goal of 0.025 mg/L in leaching tests
i) TCLP Test
The treated material prepared by Vendor A did not generally meet the goal of 0.025 mg/L mercury in the TCLP test, although one sample of the palletized material met the goal by a small margin. This behavior was generally confirmed by the CPLT, which showed similar, but generally higher, concentrations interpolated to the pH values measured in the TCLP.

The treated material prepared by Vendor B did meet the treatment goal and it did so by a substantial margin (all concentrations below 0.01 mg/L). The total mercury analysis for the material supplied by this vendor may have been high enough to support the reported waste loading (see response to question 1, above). The behavior in the TCLP was supported by similar behavior in the CPLT near the pH of the TCLP test.

The treated material prepared by Vendor C did meet the TCLP goal, but not by a substantial margin. Concentrations measured in all samples were below 0.025 mg/L, but above 0.010 mg/L. However, the reproducibility was very good, with a coefficient of determination of 9%. The behavior in the TCLP was partially confirmed by the CPLT. The concentration at the TCLP pH (pH 6.7) interpolated from data from the CPLT was similar, but somewhat higher. The interpolated concentration in the CPLT was strongly influenced by the CPLT data point at pH 6, which was somewhat lower than those measured at pH 4 and pH 8. The ability of this treated

material to reliably pass the TCLP goal is also brought into question by indications that concentrations of total mercury may have been measured in the treated material that are much lower than what would be expected from the reported waste loading (see response to question 1, above).

ii) Constant pH test
The treated material prepared by Vendor A did not meet the goal of 0.025 mg/L in the CPLT except at pH 2 (pellets and crushed samples) and pH 11 (pellets). The behavior in the CPLT was generally confirmed by that in the TCLP when concentrations are compared near the pH of the TCLP. However, interpolated concentrations in the CPLT tended to be generally higher than those measured in the TCLP.

The treated material prepared by Vendor B did meet the goal in the CPLT, except at pH 12. The behavior in the CPLT was generally confirmed by that in the TCLP when compared by interpolating CPLT data to the pH of the TCLP.

The treated material prepared by Vendor C generally did not meet the goal in the CPLT. Two samples at pH 12 had concentrations (0.0251 mg/L and 0.0249 mg/L) that were substantially the same as the treatment goal. The concentrations measured in the TCLP at pH 6.7 were similar to that measured in the CPLT at pH 6, but substantially lower than that measured at pH 8.

***Response*:** *Observations are correctly summarized.*

**Supplementary Information**

**Question 1: Are you aware of any other data/studies that are relevant to the assessment of stabilized mercury-bearing wastes and the behavior of these wastes in the environment?**

Reviewer #1: No, I am not aware of any other data/studies pertinent to this study.

Reviewer #2: This report does not have a list of references, so the question is very broad. A start would be the studies for EPA or used by EPA in previous rule-making. Second would be a literature review using appropriate keywords.

***Response:*** *A bibliography (provided by Reviewer #3) was included in a final revision of the report.*

Reviewer #3: Reviewer No. 3 provided an extensive list of articles relevant to both studies.

***Response:*** *A bibliography (provided by Reviewer #3) was included in a final revision of the report.*

**Question 2: With regard to the disposal of treated mercury wastes, are additional studies**

**warranted for other factors that impact solubility or affect ability to leach, such as use of macroencapsulation? If you believe that additional studies are needed, please explain why.**

Reviewer #1 No. This study has achieved the goals of the project and has generated scientifically sound results. This study does show that there is at least one treatment technology that should be effective over a large range of leaching fluid pH. If, however, there are additional technologies that emerge then similar testing is desirable to evaluate the expected effectiveness of the new technology.

Reviewer #2: An additional study is needed to fill the holes in this report, particularly extractions up to at least pH 12.5. If the mercuric selenide process is considered a viable technology, then mercuric selenide waste should be evaluated over the range of pH 2-12.5 and with varied chloride content in the leachate. Additional studies on other factors could be done, but the priorities seem to be: pH effects (2-12.5), chloride effects, and redox effects.

***Response****:* EPA does not agree that additional studies are warranted for this pH range, as few landfills have been shown to maintain pH conditions in excess of pH 12. EPA does agree that, if additional resources become available, it would be useful to further investigate the stability of mercuric selenide across a wider range of pH values. We also agree that varying chloride content across the pH range for all wasteforms would be a useful study, and would provide additional information on the potential effects of chloride content in landfill leachate.

Reviewer #3: These studies have adequately demonstrated that a goal of 0.025 mg/L in the TCLP can be met by existing stabilization technologies, both for a surrogate waste containing various forms of mercury at a total concentration of 5,000 mg/kg and for elemental mercury. However, meeting this goal does not insure that adequate protection of human health and the environment is assured for all conditions of waste disposal. However, this statement is not limited to mercury wastes, but is a limitation of the TCLP for all hazardous constituents. Therefore, additional studies are not warranted to determine if existing technologies can meet a TCLP goal of 0.025 mg/L for wastes that contain mercury at concentrations above 260 mg/kg. However, additional studies are warranted to develop characterization methods and analytical techniques that will insure safe disposal of hazardous wastes containing toxic materials including mercury under a range of site-specific disposal conditions.

***Response****: The additional studies proposed by the Reviewer will be considered as additional resources become available.*

**Question 3 (a): Do you agree that the following statements are supported by the research results?**

> **Site-specific disposal conditions must be considered along with appropriate treatment technology as decisions are made about disposal of mercury wastes.**

Reviewer #1: Based on the review of the results reported, it seems that pH was the only environmental parameter tested. For the Vendor B technology it appears that disposal sites with leaching fluid of greater than pH 10 should be avoided for disposing the stabilized wastes and all other sites below pH 10 will be appropriate for disposing of stabilized waste. Therefore, I believe that statement in (a) as written is more stringent than supported by the research results and should be therefore modified.

***Response:*** *pH was the only environmental variable evaluated in this study. EPA acknowledges that there are other variables, but believes that pH is certainly a significant variable. The Reviewer acknowledges that the pH of the leachate in the landfill cell, a site-specific condition, must be considered when selecting a technology. EPA believes that this supports the conclusion that "Site-specific disposal conditions must be considered along with appropriate treatment technology as decisions are made about disposal of mercury wastes."*

Reviewer #2: No. The study provides useful data on pH and chlorides, but it does not provide adequate support for an absolute requirement for site-specific data. An alternative to using site-specific conditions is a robust treatment standard which addresses the most important variables. A major implementation problem with requiring site-specific conditions is the regulatory feasibility of using site-specific information. For any disposal of hazardous wastes, treated or untreated, it is scientifically preferable to use site-specific conditions as well as the waste properties. It is misleading, however, to pursue this path unless the regulatory system has the flexibility to implement efficiently to provide the necessary protection to public health and the environment.

***Response:*** *We agree that it is scientifically preferable to use site-specific conditions as well as the waste properties to assess disposal options. EPA believes that consideration of site-specific disposal conditions along with appropriate treatment technology information is the best alternative when making environmentally sound decisions about the disposition of these high mercury stabilized wastes. As the reviewer correctly notes, implementation of such requirements into a regulatory framework would be problematic. We believe that the reviewer's suggestion of using a robust treatment standard that addresses only the most important variables would be equally problematic to implement on a national basis.*

Reviewer #3: : These research results do support this statement, because they demonstrate that pH can have an important impact on the amount of mercury leached from treated wastes. The pH of a leaching fluid can be very different under different disposal conditions. However, the research results do not prove the statement, because there could be conditions under which a waste could be characterized so that site-specific disposal conditions would not be required to insure a reasonable degree of confidence in protection of human health and the environment.

***Response:*** *EPA acknowledges the difference noted by the Reviewer between data "supporting" and "proving" a premise. The Agency does not anticipate having sufficient resources available*

*to investigate all of the characterizations conditions possible in order to definitively prove or disprove the hypothesis.*

**Question 3(b): Do you agree that the following statements are supported by the research results?**

> **The presence of chloride ions in a given disposal environment may significantly impact the release from a treated waste form (mercury selenide).**

Reviewer #1: The limited data developed and presented in this report do support the statement in (b). However, it would be desirable to generate empirical results using a number of chloride concentrations in leaching fluid to establish correlation between chloride concentrations and leachability of mercury converted to mercuric selenide. These experiments will provide a basis for deriving the lower limit of chloride concentration that should not be exceeded in the leaching fluids.

***Response**: The additional studies proposed by the Reviewer will be considered as additional resources become available.*

Reviewer #2: Yes, the data in the report do support this statement. However, there is no comparison with other variables, not even an adequate comparison with pH, which shows the relative importance of chloride concentration.

***Response**: EPA agrees that if additional studies were planned, it would be useful to further investigate mercuric selenide or elemental mercury treated to a mercuric selenide composition across a wider range of pH values. We also agree that varying chloride content across the pH range for all wasteforms would be a useful study, and would provide additional information on the potential effects of chloride content in landfill leachate.*

Reviewer #3: This statement is supported by the research results, because a leaching solution with 500 mg/L chloride did result in higher concentrations of mercury being leached at pH 7 and 10. However, the data reported is not sufficient to conclude that chloride will (rather than may) significantly impact release of mercury under a range of disposal conditions. Sufficient data exists on formation of mercury-chloride soluble complexes to strongly suggest that chloride will tend to increase mercury release, but specific conclusions on the impact of particular levels of chloride in different disposal scenarios would require additional research.

***Response**: A previously noted, EPA agrees that if additional studies were planned, it would be useful to further investigate mercuric selenide or elemental mercury treated to a mercuric selenide composition across a wider range of pH values. We also agree that varying chloride content across the pH range for all wasteforms would be a useful study, and would provide additional information on the potential effects of chloride content in landfill leachate.*

**Question 4: Do you have any other comments?**

Reviewer #1: No.

Reviewer #2: Some minor editing was needed for the final reports, i.e., spaces and placement of hyphens**.** Data on the quantities of listed wastes would have been useful to understand the magnitude of various waste treatment problems.

***Response:*** *The editorial corrections suggested by the reviewer were incorporated in a final revision to the report.*

Reviewer #3: The following corrections should be made to the report:

- (Various places) The relationship of ALTER and the University of Cincinnati should be clarified. It appears that the two are used interchangeably.
- (p. 3-2) It would be helpful to the reader to make more clear here that the "waste" being treated is elemental mercury.
- (p. 3-4, line 5 from bottom and elsewhere) Provide units for liquid/solid ratio.
- (p. 5-1, Table 5-1 and others) Percentages should be reported with no more significant digits than the measurements upon which they are based.
- (p. 5-1, Table 5-1 and others) The leaching fluid used in the TCLP tests should be specified.
- (p. 5-4, Table 5-3) Standard deviation of TCLP results for Phase II should be 0.00160.
- (p. 5-6, Figure 5-3) TCLP data are missing from this figure.

***Response:*** *The editorial corrections suggested by the reviewer were incorporated in a final revision to the report.*